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(54) Title of the Invention:

PREPREGS FOR LOW-DIELECTRIC-CONSTANT LAMINATED BOARDS

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## S P E C I F I C A T I O N

### 1. Title of the Invention:

PREPREGS FOR LOW-DIELECTRIC-CONSTANT LAMINATED BOARDS

### 2. Scope of the Patent Claim(s):

1. Prepregs for low-dielectric-constant laminated boards obtained by impregnating a base material sheet with a liquid dispersion system consisting of a fluorocarbon resin and hollow glass spheres with an average diameter of 20  $\mu\text{m}$  or less then drying the resulting impregnated base material.

2. Prepregs for low-dielectric-constant laminated boards as described in Claim 1, in which the fluorocarbon resin used includes at least one compound selected from among polytetrafluoroethylene, tetrafluoroethylene-hexafluoropropylene copolymer, tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer, and ethylene-tetrafluoroethylene copolymer.

3. Prepregs for low-dielectric-constant laminated boards as described in Claim 1 or Claim 2, in which the base material sheet is either (a), (b), or (c) as follows:

- (a) a glass fiber woven or nonwoven fabric;
- (b) an aramid fiber woven or nonwoven fabric; or
- (c) paper.

4. Prepregs for low-dielectric-constant laminated boards as described in one of Claims 1-3, in which the amount of hollow glass spheres is 5 weight% or more of the total weight of the solids contained in the prepreg.

5. Prepregs for low-dielectric-constant laminated boards as described in one of Claims 1-4, in which the hollow glass spheres are coated with a silane

coupling agent.

### 3. Detailed Description of the Invention

#### Field of Industrial Application

The present invention pertains to preregs for use in the printed-circuit board industry.

#### Conventional Techniques

The conventional base material for printed-circuit boards used in the electrical and electronics fields includes, for example, laminated boards formed by laminating preregs obtained by impregnating base materials such as glass fabric (fiber reinforcement material) with various types of resins. More specifically, glass fabric base material epoxy resin-laminated boards, glass fabric base material polyamide resin-laminated boards, glass fabric base material fluorocarbon resin-laminated boards, etc., are widely used.

#### Problems to be Solved by the Invention

For large multilayer printed-circuit boards, however, a base material with a low dielectric constant and low coefficient of thermal expansion is needed to improve its characteristics. The aforementioned glass fabric base material epoxy resin-laminated boards and the glass fabric base material polyamide resin-laminated boards described above can meet the requirement for a low coefficient of thermal expansion, but have difficulty meeting the requirement for a low dielectric constant. On the other hand, the glass fabric base material fluorocarbon resin-laminated boards mentioned above can meet the

requirement for a low dielectric constant, but their coefficient of thermal expansion in the "Z" direction is high. Therefore, when they are used as large multilayer printed-circuit boards, disconnections due to heat cycling of the sulfol-plated parts will occur easily. Namely, there is a connection reliability problem.

Many attempts have already been made to develop baseboard materials with a low dielectric constant and a low coefficient of thermal expansion. For example, in the electrical base material described in Japanese Kokai No. 63[1988]-259,907, no glass fabric base material is used. Instead, a fluoropolymer (fluorocarbon resin) with a dielectric constant-lowering effect and a ceramic filler (inorganic material) with dielectric constant-lowering and coefficient of thermal expansion-lowering effects are used to achieve the combined effect of lowering the dielectric constant and lowering the coefficient of thermal expansion of the baseboard material. However, the sheet-forming process for the electrical base material mentioned above is very complicated and expensive, which had hindered the actual use of this technique.

In contrast, the glass fabric base material fluorocarbon resin-laminated boards mentioned above can be easily formed into sheets and can be obtained by an impregnation process. Therefore, their production cost is low. Not surprisingly, the combination of (1) the aforementioned inorganic material with its dielectric constant-lowering and coefficient of thermal expansion-lowering effects and (2) fluorocarbon resins with a dielectric constant-lowering effect applied to the aforementioned glass fabric base material fluorocarbon resin-laminated boards has been proposed. Namely, during the preparation of the prepreg, which is a constituent of a laminated board, an inorganic material with dielectric constant-lowering and coefficient of thermal expansion-

lowering effects is added to a dispersed solution of fluorocarbon resin to be used for impregnating the glass fabric base material. In this way, the inorganic material together with the resin impregnate the prepreg to lower its dielectric constant and coefficient of thermal expansion.

The aforementioned inorganic materials with dielectric constant-lowering and coefficient of thermal expansion-lowering effects include, e.g., in addition to the aforementioned ceramic filler, hollow glass spheres (glass balloons) that contain sealed-in nitrogen gas, carbon dioxide, etc. Since these glass spheres are hollow, they provide even better dielectric constant-lowering and coefficient of thermal expansion-lowering effects. However, when an impregnation liquid obtained by adding hollow glass spheres to a liquid dispersion system of a fluorocarbon, etc., is used to impregnate a sheet-shaped base material such as a glass fabric to form a prepreg, most of the commercially obtainable hollow microspheres with an average sphere diameter of 40-100  $\mu\text{m}$  (see *The Development and Application of Porous Ceramics*, published by Shamshee Co., Ltd., 1984, pages 198-201) will float in the upper part of the impregnation liquid because of their low specific gravity of 0.2-0.6. In other words, these hollow glass microspheres will not disperse uniformly in the impregnation liquid. When the aforementioned base material is impregnated with a liquid like this, the glass fabric will be uniformly impregnated with the liquid but not with the hollow glass microspheres. Accordingly, it is difficult to obtain preregs with a uniform composition in a stable fashion. Moreover, the dielectric constant and coefficient of thermal expansion may vary depending on the measurement location on the prepreg. For these reasons, practical application of this method is currently unattractive.

In view of the situation described above, the present invention was de-

veloped to provide prepregs of uniform composition and stable characteristics as exemplified by a low dielectric constant and low coefficient of thermal expansion.

### An Approach to Solving the Problems

In order to solve the aforementioned problems, the prepregs for low-dielectric-constant laminated boards according to the present invention are formed by impregnating a sheet-shaped base material with a liquid dispersion system of a fluorocarbon resin and hollow glass spheres with an average sphere diameter of 20  $\mu\text{m}$  or less, then drying the resulting impregnated material.

There are no particular limitations regarding the fluorocarbon resins that can be used in the present invention. For example, polytetrafluoroethylene (to be abbreviated as PTFE in the following), tetrafluoroethylene-hexafluoropropylene copolymer (to be abbreviated as FEP in the following), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (to be abbreviated as PFA in the following), ethylene-tetrafluoroethylene copolymer (to be abbreviated as ETFE in the following), polychlorotrifluoroethylene, polyvinylidene fluoride, polyvinyl fluoride, and ethylene-chlorotrifluoroethylene copolymer can be used. Among these compounds, PTFE, FEP, PFA, and ETFE are preferable because of their low dielectric constant and high heat resistance. The aforementioned fluorocarbon resins can be used individually or in combinations of two or more.

There are no particular limitations with regard to the sheet-shaped base materials that can be used in the present invention. For example, woven or nonwoven fabrics of various fibers such as inorganic fibers made of glass, asbestos, or alumina, organic synthetic fibers made of polyester, aramid,

polyvinyl alcohol, polyacrylate, or PTFE, natural fibers such as cotton, and paper can be used. Synthetic resin films such as PTFE film, TEP film, PFA film, foamed PTFE film, polyimide film, and PPS film (= polyphenylene sulfide film) can also be used. Among these base materials, woven and nonwoven fabrics made of glass fiber or aramid fiber and paper are preferable from the standpoint of dielectric constant, heat resistance, and workability.

The average diameter of the hollow glass spheres used in the present invention must be 20  $\mu\text{m}$  or less for the following reasons.

The fluorocarbon resins used in the present invention are sparingly soluble in a solvent, therefore the impregnation of a base material with these resins is generally achieved by using them in the form of an aqueous dispersion system. The specific gravity of an aqueous fluorocarbon resin dispersion system is generally high, e.g., 1.3-1.6, and the viscosity is low, e.g., 20-30 cp (25°C). Therefore, the addition of the aforementioned commercially obtainable hollow glass spheres with their low specific gravity to the liquid suspension described above will result in flotation of the hollow glass spheres, thus making it difficult to obtain a stable impregnation liquid with uniformly dispersed hollow glass spheres. For this reason, hollow glass spheres with an average sphere diameter of 20  $\mu\text{m}$  or less are used to obtain an impregnation liquid with uniformly dispersed hollow glass spheres in a stable state. This appears to be possible because of two effects, namely, the specific gravity of the hollow glass spheres increases to approach that of the fluorocarbon resin dispersion system mentioned above, and the powders are finely pulverized. Impregnation of the aforementioned sheet-shaped material with an impregnation liquid (liquid dispersion system) that contains uniformly dispersed hollow glass spheres (and fluorocarbon resin) will result in the formation of a pre-

preg of uniform composition and with stable characteristics as exemplified by a stable low dielectric constant and a low coefficient of thermal expansion. When the average diameter of the hollow glass spheres is reduced, the compressive strength sharply improves, therefore breakage of the hollow glass spheres by the bonding pressure during prepreg lamination and formation of the boards can be prevented.

There are no particular limitations with regard to the lower limit of the sphere diameter of the hollow glass spheres. However, it is difficult to reduce the wall thickness of a hollow glass sphere below  $0.5\text{ }\mu\text{m}$ , therefore the sphere diameter is preferably set at greater than  $1.5\text{ }\mu\text{m}$  in order to take advantage of the dielectric constant-lowering effect of these hollow glass spheres.

The ratio of the hollow volume of hollow glass spheres with an average sphere diameter of  $20\text{ }\mu\text{m}$  or less to the volume of the entire sphere is smaller than that of hollow glass spheres with an average sphere diameter of  $40\text{-}100\text{ }\mu\text{m}$ , but their dielectric constant-lowering and coefficient of thermal expansion-lowering effects are still present after they are made into a complex.

There are no particular limitations with regard to the methods that can be used to manufacture the hollow glass spheres, the types of glass that can be used as a structural material for the walls, and the types of gases that can be sealed into the hollow portions.

There are no particular limitations with regard to the amount of hollow glass spheres in the prepreg, but in order to obtain distinctive dielectric constant-lowering and coefficient of thermal expansion-lowering effects, the content is preferably 5 weight% or more, and especially 15-50 weight% of the

total solids content of the prepreg. When the amount of hollow glass spheres exceeds 50 weight%, the content of fluorocarbon resin in the prepreg will decrease and voids will form more easily during the lamination process. This possibility should be carefully considered. Although there are no particular limitations with regard to the coating of the hollow glass spheres, they are preferably coated with a silane coupling agent, because coating can reduce the amount of water absorption of the prepreg as well as the laminated board obtained by lamination of the prepreps. There are no particular limitations with regard to the coating method used, e.g., dry coating, wet coating, etc., can be used.

There are no particular limitations with regard to the silane coupling agents that can be used in the present invention, e.g., phenyltrimethoxysilane, trifluoropropyltrimethoxysilane,  $\gamma$ -(2-aminoethyl)aminopropyltrimethoxysilane, etc., can be used individually or in mixtures of 2 or more.

The prepreps for low dielectric constant laminated boards of the present invention can be laminated with, for example, a metal foil and used as a metal foil-clad laminated board. Similarly, the prepreps can be used as adhesive sheets or as sealing material during the manufacture of multilayer printed-circuit boards.

#### Functions

When hollow glass spheres with an average sphere diameter of 20  $\mu\text{m}$  or less are used, their specific gravity will be higher and will thus approach the specific gravity of the fluorocarbon resin liquid dispersion system. In addition, there will be a fine pulverization effect on the powder which will promote a uniform dispersion of the hollow glass spheres in the liquid disper-

sion system of fluorocarbon resin. The liquid dispersion system in which the hollow glass spheres and fluorocarbon resin are dispersed uniformly is used to impregnate the sheet-shaped base material, which is then dried. In this way, the base material can be impregnated uniformly with a fluorocarbon resin that has a dielectric constant-lowering effect and hollow glass spheres that have dielectric constant-lowering and coefficient of thermal expansion-lowering effects. A prepreg thus obtained will have a uniform composition and stable characteristics due to its low dielectric constant and low coefficient of thermal expansion.

#### ACTUAL EXAMPLES

Actual examples of the present invention and comparison examples will now be presented, however the present invention is not limited in any way to these examples.

##### Actual Example 1

150 weight parts of hollow glass spheres all with diameters of 40  $\mu\text{m}$  or less and with an average sphere diameter of 13  $\mu\text{m}$  (H-330; a product of the Silica Kogyo Co.) was added to 500 weight parts of an aqueous dispersion system containing 60 weight% of PTFE (D-2; a product of the Daikin Kogyo Co.) and the mixture was stirred thoroughly.

The resulting liquid dispersion system of PTFE and hollow glass spheres did not separate into two layers after standing for 1 hour, i.e., the PTFE and the hollow glass spheres remained uniformly dispersed in the system in a stable manner.

This liquid dispersion system of PTFE and hollow glass spheres was used

to impregnate ( $97 \text{ g/m}^2$ ) a glass fabric made of E glass fibers. After the impregnation process, the fabric was drawn through a narrow gap formed by 2 rolls, dried at  $150^\circ\text{C}$  for 5 minutes, then dried further at  $380^\circ\text{C}$  for 5 minutes. The cloth was impregnated again with the aforementioned liquid dispersion system of PTFE and hollow glass spheres and then dried. These processes were repeated to obtain a prepreg in which the amount of glass fabric was 25 weight% of the total solids content of the prepreg.

Four prepreps obtained in this way were stacked and copper foil  $35\text{-}\mu\text{m}$  thick was pasted on the top and bottom of the stack. The composite product was then placed in a mold and molded at a pressure of  $30 \text{ kg/cm}^2$  and a temperature of  $380^\circ\text{C}$  for 1 hour to obtain a composite laminated board clad on both sides with copper foil.

The physical properties of the resulting composite laminated board clad on both sides with copper foil, such as the dielectric constant, tangent of loss angle, coefficient of thermal expansion, and amount of water absorption were then determined. The coefficient of thermal expansion was measured in the thickness direction in a temperature range of  $30\text{-}200^\circ\text{C}$ . The amount of water absorption was determined as the percent increase in the weight of the laminated board after immersing it in warm water ( $50^\circ\text{C}$ ) for 48 hours (D-48/50). The results obtained are given in Table 1.

#### Actual Example 2

Hollow glass spheres with an average sphere diameter of  $20 \mu\text{m}$  were obtained by size-grading hollow glass spheres with an average sphere diameter of  $55 \mu\text{m}$  (SI; a product of W. R. Grace Co.) and were used in place of the hollow glass spheres with an average sphere diameter of  $13 \mu\text{m}$  used in Actual Example

1. The other procedures used to prepare the liquid dispersion system of PTFE and hollow glass spheres were the same as those used in Actual Example 1.

The resulting liquid dispersion system did not separate into 2 layers after standing for 1 hour, i.e., the PTFE and hollow glass spheres remained uniformly dispersed in the system in a stable manner.

This liquid dispersion system of PTFE and hollow glass spheres was used to prepare preregs as described in Actual Example 1.

The preregs thus obtained were used to prepare a composite laminated board clad on both sides with copper foil as described in Actual Example 1.

The physical properties of the resulting composite laminated board clad on both sides with copper foil were determined as described in Actual Example 1. The results obtained are given in Table 1.

### Actual Example 3

A liquid dispersion system of PTFE and hollow glass spheres was prepared as described in Actual Example 1, except that the amount of hollow glass spheres contained in the liquid dispersion system of PTFE and hollow glass spheres was changed to 60 weight%.

The resulting liquid dispersion system did not separate into 2 layers after standing for 1 hour, i.e., the PTFE and hollow glass spheres remained uniformly dispersed in the system in a stable manner.

This liquid dispersion system of PTFE and hollow glass spheres was used to prepare preregs as described in Actual Example 1.

The preregs thus obtained were used to prepare a composite laminated board clad on both sides with copper foil as described in Actual Example 1.

The physical properties of the resulting composite laminated board clad

on both sides with copper foil were determined as described in Actual Example 1. The results obtained are given in Table 1.

#### Actual Example 4

150 weight parts of hollow glass spheres with an average sphere diameter of 13  $\mu\text{m}$  were added to a solution obtained by dissolving 1.5 weight parts of a silane coupling agent (phenyltrimethoxysilane; KBM 103; a product of the Shinetsu Kagaku Kogyo Co.) in 250 weight parts of methyl alcohol. The mixture was stirred thoroughly and the methyl alcohol was removed by vacuum distillation at room temperature to obtain hollow glass spheres coated with a silane coupling agent.

The silane coupling agent-coated hollow glass spheres mentioned above were used in place of the hollow glass spheres used in Actual Example 1 to prepare a liquid dispersion system of PTFE and hollow glass spheres as described in Actual Example 1.

The resulting liquid dispersion system did not separate into 2 layers after standing for 1 hour, i.e., the PTFE and hollow glass spheres remained uniformly dispersed in the system in a stable manner.

This liquid dispersion system of PTFE and hollow glass spheres was used to prepare preregs as described in Actual Example 1.

The preregs thus obtained were used to prepare a composite laminated board clad on both sides with copper foil as described in Actual Example 1.

The physical properties of the resulting composite laminated board clad on both sides with copper foil were determined as described in Actual Example 1. The results obtained are given in Table 1.

#### Comparison Example 1

Hollow glass spheres with an average sphere diameter of 40  $\mu\text{m}$  were obtained by size-grading hollow glass spheres with an average sphere diameter of 55  $\mu\text{m}$  (SI; a product of the W. R. Grace Co.) and were used in place of the hollow glass spheres with an average sphere diameter of 13  $\mu\text{m}$  used in Actual Example 1 to prepare a liquid dispersion system of PTFE and hollow glass spheres as described in Actual Example 1.

The resulting liquid dispersion system separated into 2 layers after standing for 1 hour, i.e., the hollow glass spheres floated.

This liquid dispersion system was used to impregnate a glass fabric, but the state of adhesion of the hollow glass spheres to the glass cloth could not be stabilized, therefore the hollow glass sphere content of the prepreg varied from one location to another. Accordingly, stable characteristics could not be determined.

#### Comparison Example 2

Prepregs were prepared as described in Actual Example 1, except that the glass fabric was impregnated with 500 weight parts of the aqueous dispersion system containing 60 weight% of PTFE (D-2; a product of the Daikin Kogyo Co.) used in Actual Example 1, but no hollow glass spheres. The resulting dispersion system of PTFE did not separate into 2 layers after standing for 1 hour, i.e., the PTFE remained uniformly dispersed in the system in a stable manner.

This liquid dispersion system was used to prepare prepregs, which were then used to prepare a composite laminated board clad on both sides with copper foil as described in Actual Example 1.

The physical properties of the resulting composite laminated board clad on both sides with copper foil were determined as described in Actual Example 1. The results obtained are given in Table 1.

#### Comparison Example 3

A glass fabric made of E glass fibers was impregnated with polyimide resin to obtain a prepreg that contained 48 weight% of the glass cloth based on the total weight of the solids in the prepreg (R-4670; a product of the Matsushita Denko Co.). Four of these prepreps were laminated and copper foil 35- $\mu\text{m}$  thick was pasted on both sides of the laminated prepreps thus obtained. This composite product was then placed in a mold and molded at a pressure of 30 kg/cm<sup>2</sup> and a temperature of 210°C for 2 hours to obtain a composite laminated board clad on both sides with copper foil.

The physical properties of the resulting composite board clad on both sides with copper foil were determined as described in Actual Example 1. The results obtained are given in Table 1.

TABLE 1. KEY: (a) Actual Example .... ; (b) Comparison Example .... ; (c) stability of uniform dispersion of impregnation liquid; (d) hollow glass spheres; (e) resin; (f) amount of glass fabric in the prepreg, wt.%; (g) physical properties of the composite laminated board clad on both sides with copper foil; (h) average sphere diameter,  $\mu\text{m}$ ; (i) amount in the prepreg, wt.%; (j) kind; (k) amount in prepreg, wt.%; (l) dielectric constant, 1 MHz, normal state; (m) tangent of loss angle, 1 MHz, normal state; (n) coefficient of thermal expansion,  $\times 10^{-6}/^{\circ}\text{C}$ ; (o) water absorption, %; (p) did not separate into 2 layers after standing for 1 hour; (q) separated into 2 layers after standing for 1 hour (unstable); and (r) polyimide resin.

	(c) 含浸液の均一分散の安定性	(d) 中空ガラス球		(e) 樹脂		(f) プリプレグ中のガラス含有量 (重量%)	(g) 両面銅箔張り層板の物性			
		平均粒径 (h)	プリプレグ中の含有量 (重量%) (i)	種類 (j)	プリプレグ中の含有量 (重量%) (k)		誘電率 (1MHz, 常温) (l)	損失正接 (1MHz, 常温) (m)	熱膨張係数 ( $\times 10^{-6}/^{\circ}\text{C}$ ) (n)	吸水率 (%) (o)
(a) 実例1	静置1日後二層に分離せず(p)	13	25	PTFE	50	25	2.65	0.0020	60	0.20
(a) 実例2	静置1日後二層に分離せず(p)	20	29	PTFE	46	25	2.60	0.0035	55	0.22
(a) 実例3	静置1日後二層に分離せず(p)	13	5	PTFE	70	25	2.55	0.0012	105	0.14
(a) 実例4	静置1日後二層に分離せず	13	25	PTFE	50	25	2.65	0.0010	60	0.10
(b) 比較例1	静置1日後二層に分離した (安定性なし) (q)	40	—	PTFE	—	—	—	—	—	—
(b) 比較例2	静置1日後二層に分離せず	—	0	PTFE	75	25	2.60	0.0006	150	0.09
(b) 比較例3	—	—	0	ポリイミド樹脂 (r)	52	48	4.50	0.0080	60	0.50

It can be seen from Table 1 that the values of the dielectric constant, tangent of loss angle, and coefficient of thermal expansion of the laminated boards obtained from Actual Examples 1-4 were all lower than those of the laminated boards obtained from Comparison Examples 2 and 3. A comparison of the amount of water absorption of the laminated boards obtained from Actual Examples 1 and 4 revealed that the amount of water absorption could be reduced by coating the hollow glass spheres with a silane coupling agent.

### Effects of the Invention

The preregs of the present invention show stable characteristics as exemplified by a low dielectric constant and low coefficient of thermal expansion. Laminated boards obtained by laminating these preregs therefore have excellent characteristics which are exemplified by a low dielectric constant and low coefficient of thermal expansion. The preregs of the present invention, therefore, can be a very useful material in the field of large multi-layer printed-circuit boards.

In addition, the aforementioned preregs can be obtained by an impregnation process that does not require complicated devices or procedures, therefore the cost of production can be kept low.

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